

# PATENT SPECIFICATION

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NO DRAWINGS

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## (54) EMULSIONS

(71) We, L'OREAL, a French Body Corporate of 14 Rue Royale 75, Paris 8e, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to emulsions of the "water-in-oil" and "oil-in-water" type.

It has already been proposed to produce cosmetic products such as make-up or beauty creams which are in the form of "water-in-oil" emulsions because the water retained in the dispersed state in the oily phase ensures, in certain cases, better moisturisation of the epidermis and better protection of the latter. However, it has hitherto been difficult to market cosmetic products of this type because such "water-in-oil" emulsions generally display two sorts of difficulties:

First of all, it is necessary that the emulsions should not invert, i.e. they should not convert into an emulsion of the "oil-in-water" type by dilution with water.

Furthermore, it is necessary that such cosmetic products should be sufficiently stable to retain their finely dispersed state, regardless of the period of storage (which can be several years), and regardless of major variations in temperature which generally favour destruction of the emulsion through loss of the aqueous phase from the dispersed state, which furthermore is a particular hazard where the emulsions are subjected to low temperatures.

With this in mind, the Applicant Company has already proposed to use, as the emulsifier in such emulsions, a mixture of an oxypropylenated-polyglycerolated alcohol and of magnesium isostearate, succinate esters of polyoxyalkylenated fatty alcohols, or oxypropylenated-oxyethyleneated alcohols.

Furthermore, it is already known to use, as emulsifiers in cosmetic compositions, in particular creams, polymers consisting of a sequence obtained by polymerisation of propylene oxide, to which have been grafted two sequences obtained by polymerisation of ethylene oxide. Such copolymers are known under the name of Pluronics (sold by Messrs. Wyandotte Chem. Corp.).

The Applicant Company has now found, surprisingly, that it is possible to produce very good cosmetic emulsions by using a large variety of certain types of sequence polymers as the emulsifier.

Such polymers are known and some of them have already been proposed as additives in motor lubricants.

It is well known that the various monomers involved in the production of copolymers can behave in different ways in the formation of the polymer chain, and in general polymerisation processes make it possible to slant the reaction towards producing one or another type of polymer. In particular, with a well-defined polymerisation process it is possible to obtain copolymers wherein the monomer units are grouped according to types, these groupings being described by the name of "sequence". Such copolymers are defined herein as "sequence copolymers".

The sequence polymers are generally binary polymers containing two types of sequence, each made up from identical monomers. The number of sequences is generally two or three.

The copolymers containing two sequences are called "bisequence" copolymers, and the distribution of the monomer units in the polymer chain can be represented as follows:



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The copolymers containing three sequences are generally called "trisequence" copolymers and the distribution of the monomer units in the polymer chain can be represented as follows:



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The present invention provides an emulsion which can be used in cosmetics, of the "water-in-oil" type, which is stable and cannot readily be inverted; it contains, as the emulsifier, a sequence polymer simultaneously containing at least one lipophilic sequence and at least one hydrophilic sequence.

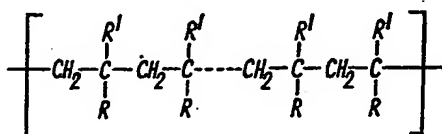
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The lipophilic sequences are obtained from monomers with lipophilic chains, whilst the hydrophilic sequences are obtained from monomers with hydrophilic chains.

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The lipophilic sequences of the sequence polymers used in the emulsions of this invention can be represented by the following formula:

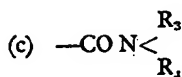
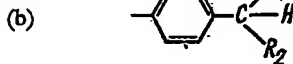
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in which

R is selected from the group consisting of

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... R' representing a hydrogen atom

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... R' representing a methyl radical

each of R<sub>1</sub> and R<sub>2</sub>, which may be identical or different, represents either a hydrogen atom or an alkyl radical with 1 to 4 carbon atoms,

R<sub>3</sub> represents a saturated hydrocarbon chain of 6 to 18 carbon atoms,

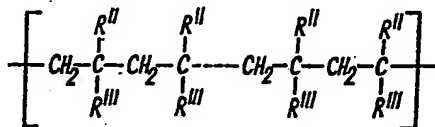
R<sub>4</sub> represents a methyl or ethyl radical and

R<sub>5</sub> represents a saturated hydrocarbon chain of 5 to 26 carbon atoms.

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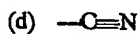
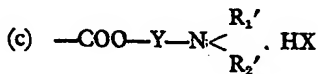
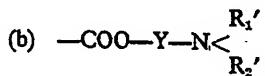
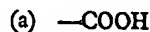
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The hydrophilic sequences of the sequence polymers used in the emulsions of this invention can be represented by the following formula:

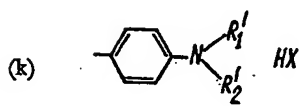
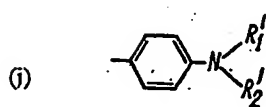
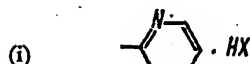


in which:

$R''$  is selected from the group consisting of:



$R'''$  representing a methyl radical



$R'''$  representing a hydrogen atom

5 each of  $R_1'$  and  $R_2'$ , which may be identical or different, represents either a hydrogen atom or an alkyl radical with 1 to 4 carbon atoms,  
Y represents a saturated hydrocarbon chain of 2 to 4 carbon atoms or a hydrocarbon chain of 2 to 4 carbon atoms interrupted by hetero-atoms such as oxygen and sulphur,  
and

10 HX represents an inorganic or organic acid taken from the group consisting of hydrochloric acid, hydrobromic acid, lactic and acetic acid.

If  $R''$  represents a carboxylic acid group, this group can be neutralised with an inorganic or organic base, such as ammonia, monoethanolamine, diethanolamine, triethanolamine, the isopropylamines, morpholine, 2-amino-2-methyl-propanol-1, or 2-

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amino-2-methyl-propanediol-1,3, or be salified in the form of a sodium, potassium or magnesium salt.

Amongst the monomers which can lead to the formation of lipophilic sequences, the following may be quoted: styrene, 4-methyl-styrene and lauryl methacrylate.

Amongst the monomers which can lead to the formation of hydrophilic sequences, the following may be quoted: 2-vinyl-pyridine, its hydrochloride and its lactate; 4-vinyl-pyridine, its hydrochloride and its lactate; *para*-dimethylamino-styrene, its hydrochloride and its lactate; 2-(N,N-dimethylamino)-ethyl methacrylate; 2-(N,N-diethylamino)-ethyl methacrylate, 2-(N,N-dimethylamino)-ethyl-glycol methacrylate, 2-(N,N-diethylamino)-ethyl-glycol methacrylate; methacrylonitrile.

In an alternative embodiment, the hydrophilic sequences containing the tertiary amine groups are quaternised by means of a quaternising agent chosen, for example, from dimethyl sulphate, ethyl bromide or  $\beta$ -bromoethanol.

The molecular weights of the sequence polymers used according to the invention can vary within wide limits. They are generally fixed as a function of the properties desired of the emulsifier.

The sequence polymers according to the present invention generally have a molecular weight of between 1,000 and 1,000,000, but preferably between 8,000 and 700,000.

Equally, the ratio of the lengths of the sequences can vary within very wide limits and is generally decided by the application for which the copolymer is destined, namely either a "water-in-oil" emulsion or "oil-in-water" emulsion.

In effect, the sequence polymers used according to the present invention can also be used to produce "oil-in-water" emulsions if the sequence polymer is soluble in water whilst having a certain affinity towards oils.

One of the most characteristic and the most important properties of the sequence polymers is that each of the sequences displays the properties of the corresponding homopolymer. Depending on the choice of the sequences, it is possible to obtain sequence copolymers which are simultaneously hydrophilic and lipophilic, but of which the hydrophilic or lipophilic character is more or less marked.

The present invention also provides a cosmetic composition or an excipient for a pharmaceutical product, which comprises an emulsion of the present invention.

The proportion of emulsifier in the emulsion according to the invention can vary within very wide limits, for example from 5 to 20% by weight, whilst the proportion of water can vary from about 20 to 75% by weight relative to the total weight of the constituents.

In general, the proportion of emulsifier relative to the mixture of oil+wax is at least 10% by weight.

The proportion of the mixture of oil+wax relative to the total weight of the emulsion according to the invention is generally between 20 and 65% by weight.

According to the invention, a large variety of products can be used to form the oily phase of the emulsions, such as:

hydrocarbon oils, such as paraffin oil, stringy "Vaseline" (Registered Trade Mark, i.e. partially flowing paraffin), perhydro-squalene and solutions of microcrystalline wax in paraffin oil and Purcellin oil.

animal or vegetable oils, such as caballine oil, pork fat, sweet almond oil, calophyllum oil, olive oil and avocado oil, these being oils which are well absorbed by the skin but which can in certain cases give rise to rancidity;

saturated esters which cannot turn rancid and have good penetrating ability, such as isopropyl palmitate, isopropyl myristate, ethyl palmitate, diisopropyl adipate and the triglycerides of octanoic and decanoic acids.

Silicone oils which are soluble in other oils or phenyl-ethyl alcohol can also be added to the oily phase.

In certain cases it is possible to utilise waxes such as carnauba wax, candellila wax, beeswax, microcrystalline wax and ozokerite to assist retention of the oils.

Long-chain fatty alcohols, such as the fatty alcohol from beeswax, cholesterol, lanolin alcohol or magnesium stearate can also be used as adjuvants to the oily phase.

The emulsions according to the invention make it possible to produce the most diverse cosmetic products, such as moisturising creams, foundation creams, make-up, fluid creams, brilliantines and products for protection against sunburn.

A further subject of the present invention is a process for the preparation of "water-in-oil" and "oil-in-water" emulsions from emulsifiers consisting of the sequence polymers defined above.

This process of preparation is essentially characterised by the fact that in a first stage the sequence copolymer is mixed with the "oil" phase with vigorous stirring and

at a temperature of about 150°C and that, in a second stage, after having cooled the sequence copolymer+oil/wax mixture to a temperature of about 80°C, the "water" phase, with or without the addition of hydrochloric, lactic or acetic acid, and previously heated to the same temperature, is introduced into it, after which the mixture is cooled to ambient temperature, whilst stirring. At the end of the operation, the emulsion can be passed through a (triple) roll mill to refine it.

Though the process for the preparation of the sequence polymers is known in general we will review the principal stages involved.

These polymerisations are generally initiated by so-called "anionic" initiators, which are generally metals belonging to the first group of the periodic table of the elements, such as lithium, sodium and potassium, or organic compounds of these metals. Compounds such as diphenyl-methyl-sodium, fluorenyl-lithium, fluorenyl-sodium, naphthalene-sodium, naphthalene-potassium, naphthalene-lithium, tetraphenyl-disodiobutane and phenyl-isopropyl-potassium may, for example, be mentioned.

The choice of the polymerisation initiators is in fact very important, because it allows the structure of the sequence polymer to be decided. Thus, naphthalene-sodium allows the polymerisation to be directed towards obtaining a "tri-sequence" copolymer. On the other hand, phenylisopropyl-potassium allows the polymerisation to be directed towards obtaining a "bi-sequence" polymer.

These polymerisation reactions leading to the formation of sequence polymers take place in aprotic solvents such as, for example, benzene, tetrahydrofuran and toluene.

In general terms, tri-sequence polymers, for example, are obtained as follows. First of all, a solution of the initiator in the selected solvent is prepared, and then one of the monomers which is to give rise to one of the sequences is added; after polymerisation of this monomer (this polymerisation taking place in the space of a few minutes), the second monomer which is to give rise to the formation of the two other sequences is added, and these two other sequences arrange themselves symmetrically relative to the sequence of the first monomer. After the end of the polymerisation, the tri-sequence polymer can be deactivated by means of a few drops of methanol.

In general, the reaction leading to the formation of these sequence polymers is carried out at a temperature of about -70°C. These polymerisation reactions aimed at the production of sequence polymers can obviously not be carried out with monomers containing mobile hydrogens, such as acids and amides.

Hence, if it is desired to obtain sequence polymers containing acid or amide groups in one of their sequences, it is necessary to start from monomers which can subsequently, through chemical reaction, give rise to this type of group. For example, it is possible, for this purpose, to start from monomers possessing a nitrile group or an ester group. In effect, it is possible to obtain the corresponding acids by hydrolysis, and subsequently to obtain the corresponding amides by amidification.

Such a procedure can be used if it is desired to obtain lipophilic sequences consisting of methacrylamide radicals or hydrophilic sequences consisting of methacrylic acid radicals.

The following Examples further illustrate the present invention. Example 1 illustrates the preparation of the sequence polymers.

#### EXAMPLE 1.

Preparation of a bisequence polymer of 2-vinylpyridine and lauryl methacrylate

One litre of anhydrous distilled tetrahydrofuran is introduced into a flask of two litres capacity equipped with a mechanical stirrer, two dropping funnels, a graduated tube, a nitrogen inlet tube, a dip tube which allows samples of the reaction mixture to be taken during the reaction, and a thermometer. The flask is then cooled to a temperature of -70°C by means of a mixture of solid carbon dioxide and methanol.

The whole of the apparatus is under a nitrogen atmosphere, which apparatus has been carefully purified by heating to 400°C in the presence of copper foil, and the stream of nitrogen is also purified by passing over anhydrous potassium hydroxide and over anhydrous magnesium perchlorate.

A solution of diphenyl-methyl-sodium in anhydrous distilled tetrahydrofuran is added dropwise by means of the graduated tube, whilst stirring. At the start of the addition, the diphenyl-methyl-sodium solution loses its colour as soon as it comes into contact with the tetrahydrofuran of the flask. The introduction of the diphenyl-methyl-sodium solution is then continued until a reddish-yellow colour persists in the reaction flask. A further 2.82 ml of a solution containing 247 mg of diphenyl-methyl-

sodium in tetrahydrofuran are then introduced through the same graduated tube, the whole being under a nitrogen atmosphere.

30.3 g of carefully purified 2-vinylpyridine are introduced rapidly into the flask by means of one of the dropping funnels, under nitrogen and whilst stirring.

The temperature inside the flask rises to  $-62^{\circ}\text{C}$  for a few minutes, whilst the colour of the reaction mixture becomes darker.

A small amount of solution of "living" polymer of 2-vinylpyridine in tetrahydrofuran is removed by suction, using the dip tube, and is employed for calculating its molecular weight.

When the internal temperature of the flask drops again, 22.4 g of carefully purified lauryl methacrylate are rapidly introduced into the flask by means of the other dropping funnel, under nitrogen. The temperature rises to  $-62^{\circ}\text{C}$  and when the exothermicity of the polymerisation subsides, the "bisequence" polymer, in which the two sequences consist of poly(lauryl methacrylate) and poly-2-vinylpyridine, is deactivated. In general, this last stage is carried out by means of a few drops of methanol. The solution then becomes practically colourless, the tetrahydrofuran is distilled, and the residual polymer dissolved in chloroform and then precipitated by means of petroleum ether. After twice dissolving in chloroform and twice precipitating with petroleum ether, the polymer is dried under reduced pressure.

30 g of dry polymer (yield, 60%) are thus obtained. The molecular weight of this copolymer, determined by the light scattering method in solution in methanol, is:

$$\overline{M}_p = 110,000, d_n/d_c (\text{MeOH}) = 0.134.$$

The sample of the homopolymer of poly-2-vinylpyridine, once it has been deactivated with methanol and purified in accordance with the method used for the purification of the bisequence polymer, can be used to determine its molecular weight in the same way:

$$\overline{M}_p = 60,000, d_n/d_c (\text{MeOH}) = 0.236.$$

The sequence polymers shown in Tables I and II below were prepared in accordance with the procedure as described above.

### EXAMPLES OF COMPOSITIONS

#### EXAMPLE A:

A fluid cream of the following composition is prepared in accordance with the invention:

|                      |      |
|----------------------|------|
| Copolymer No. 3      | 7 g  |
| Paraffin oil         | 40 g |
| Microcrystalline wax | 3 g  |
| Water                | 50 g |

#### EXAMPLE B:

A foundation cream of the following composition is prepared in accordance with the invention:

|                                  |        |
|----------------------------------|--------|
| Copolymer according to Example 1 | 7.4 g  |
| Paraffin oil                     | 20 g   |
| Perhydrosqualene                 | 24 g   |
| Titanium oxide                   | 1.5 g  |
| Ochre                            | 1.5 g  |
| Perfume                          | 0.2 g  |
| Water+lactic acid (3.4 g)        | 45.4 g |

#### EXAMPLE C:

A night cream of the following composition is prepared according to the invention:

|                                  |        |
|----------------------------------|--------|
| Copolymer according to Example 1 | 7 g    |
| Paraffin oil                     | 22.1 g |
| Isopropyl palmitate              | 10 g   |
| Purcellin oil                    | 12 g   |
| Bleached ozokerite               | 2.5 g  |
| Water+hydrochloric acid (1.4 g)  | 46.4 g |

TABLE I  
"Bisequence" Polymer

| Copolymer No. | Monomer 1                              | Monomer 2                | Amount<br>1 2<br>(g) | Catalyst solution in THF (ml) | Amount of catalyst (mg) | Yield % | Average molecular weight | $\frac{dn}{dc}$ (THF) | Elementary analysis %     | L/H in weight in the copolymer |
|---------------|--|--------------------------|----------------------|-------------------------------|-------------------------|---------|--------------------------|-----------------------|---------------------------|--------------------------------|
| 2             | 2-Vinylpyridine (H)                    | Lauroyl methacrylate (L) | 30 15                | 20                            | 1,632(a)                | 45      | 967,000                  | 0.113                 | C 73<br>H 9.6<br>N 4.5    | 66/34                          |
| 3             | 2-Dimethylamino-ethyl methacrylate (H) | " (L)                    | 7 12.5               | 30                            | 4,400(a)                | 41      | 8,000                    | 0.079                 | C 74.4<br>H 11.6<br>N 0.9 | 90/10                          |
| 4             | " (H)                                  | " (L)                    | 7 12.5               | 6                             | 430(a)                  | 15.8    | 109,000                  | 0.079                 | C 74.5<br>H 11.4<br>N 0.9 | 90/10                          |
| 5             | " (H)                                  | " (L)                    | 7 27.5               | 6                             | 430(a)                  | 32      | 254,000                  | 0.079                 | C 74.5<br>H 11.4<br>N 0.8 | 91/9                           |
| 6             | Styrene (L)                            | 2-Vinylpyridine (H)      | 7 5                  | 25                            | 1,260(b)                | 67      | 15,400                   | 0.181                 | C 87.9<br>H 7.6<br>N 4.1  | 31/69                          |
| 7             | " (L)                                  | " (Y)                    | 7 10                 | 25                            | 1,260(b)                | 80      | 270,000                  | 0.182                 | C 85.1<br>H 7.5<br>N 6.6  | 50/50                          |

N.B.: The letter "L" signifies *lipophilic*  
The letter "H" signifies *hydrophilic*  
(a) Diphenyl-methyl-sodium  
(b) Phenyl-isopropyl -potassium

The preparation of the above "bisequence" copolymers is carried out by homopolymerisation of the monomer 1, followed by copolymerisation of homopolymer with the monomer 2.

TABLE  
"Trisequence"

| Copolymer No. | Monomer 1               | Monomer 2                               | Type of copolymer | Quantity |     | Catalyst solution in THF (ml) |
|---------------|-------------------------|---|-------------------|----------|-----|-------------------------------|
|               |                         |   |                   | 1        | 2   |                               |
|               |                         |   |                   | (g)      |     |                               |
| 8             | Styrene (L)             | 2-Vinyl pyridine (H)                    | H-HL-LH-H         | 20       | 5   | 12                            |
| 9             | " (L)                   | " (H)                                   | H-HL-LH-H         | 20       | 13  | 12                            |
| 10            | " (L)                   | " (H)                                   | H-HL-LH-H         | 20       | 30  | 12                            |
| 11            | 4-Methyl styrene (L)    | 4-Vinyl-pyridine (H)                    | H-HL-LH-H         | 6        | 1.5 | 3                             |
| 12            | " (L)                   | " (H)                                   | H-HL-LH-H         | 6        | 4   | 3                             |
| 13            | Styrene (L)             | 2-Dimethyl amino-ethyl methacrylate (H) | H-HL-LH-H         | 20       | 5   | 12                            |
| 14            | " (L)                   | " (H)                                   | H-HL-LH-H         | 20       | 13  | 12                            |
| 15            | " (L)                   | " (H)                                   | H-HL-LH-H         | 20       | 30  | 12                            |
| 16            | 2-Vinyl-pyridine (H)    | Lauryl methacrylate (L)                 | L-LH-HL-L         | 11       | 5   | 6                             |
| 17            | " (H)                   | " (L)                                   | L-LH-HL-L         | 11       | 11  | 6                             |
| 18            | Lauryl methacrylate (L) | 2-Dimethyl-amino-ethyl methacrylate (H) | H-HL-LH-H         | 5        | 2   | 6                             |
| 19            | " (L)                   | " (H)                                   | H-HL-LH-H         | 5        | 5   | 6                             |
| 20            | Styrene (L)             | 4-Vinyl-pyridine (H)                    | H-HL-LH-H         | 5        | 3   | 3                             |
| 21            | " (L)                   | " (H)                                   | H-HL-LH-H         | 5        | 10  | 3                             |
| 22            | " (L)                   | 2-Dimethyl-aminoethyl methacrylate (H)  | H-HL-LH-H         | 20       | 2   | 12                            |

N.B. The preparation of the above "trisequence" copolymers is carried out by homopolymerisation of the monomer 1, followed by copolymerisation of the homopolymer with the monomer 2. "L" denotes "lipophilic" and "H" denotes "hydrophilic".



## II

## Copolymer

| Amount<br>of<br>catalyst<br>(mg)<br>naphthalene<br>sodium | Yield<br>% | Average<br>molecular<br>weight | $\frac{dn}{dc}$<br>(THF) | Elementary<br>analysis |     |     | L/H <sub>2</sub> by<br>weight<br>in the<br>copolymer |
|---|------------|--------------------------------|--------------------------|------------------------|-----|-----|--|
|   |            |                                |                          | C                      | H   | N   |  |
| 543   | 80         | 52,000                         | 0.182                    | 91.3                   | 9.0 | <1  | >93/7  |
| 543   | 76         | 57,000                         | 0.174                    | 84.1                   | 7.3 | 7.7 | 42/58  |
| 543   | 74         | 50,000                         | 0.178                    | 89.5                   | 7.8 | 2.4 | 82/18  |
| 408   | 40         | 55,000                         | 0.183                    | 91                     | 8   | <1  | >93/7  |
| 408   | 35         | 71,000                         | 0.167                    | 89.7                   | 8   | 1.3 | 89.9/9.1   |
| 543   | 60         | 78,000                         | 0.153                    | 82.5                   | 8.5 | 2.6 | 71/29  |
| 543   | 55         | 196,000                        | 0.142                    | 77.3                   | 8.5 | 2.6 | 58.5/41.5  |
| 543   | 50         | 202,000                        | 0.131                    | 74.5                   | 7.0 | 4.5 | 49.5/50.5  |
| 816   | 50         | 40,000                         | 0.150                    | 76.4                   | 9.5 | 5.3 | 61/39  |
| 816   | 41         | 46,000                         | 0.116                    | 76.4                   | 9.7 | 5.4 | 60/40  |
| 816   | 20         | 730,000                        | 0.082                    | 58.9                   | 9.2 | 6.8 | 27/75  |
| 816   | 40         | 880,000                        | 0.080                    | 61.4                   | 9.8 | 7.4 | 17/83  |
| 407   | 44         | 66,000                         | 0.189                    | 92.2                   | 7.5 | <1  | >92.5/7.5  |
| 407   | 27         | 65,008                         | 0.195                    | 92.7                   | 7   | <1  | >92.5/7.5  |
| 543   | 60         | 78,000                         | 0.153                    | 82.5                   | 8.5 | 2.6 | 71/29  |

## EXAMPLE D:

A milk of the following composition is prepared according to the invention:

|   |  |      |   |
|---|--|------|---|
|   | Copolymer No. 4                            | 12 g |   |
|   | Paraffin oil                               | 18 g |   |
| 5 | Stringy vaseline                           | 8 g  | 5 |
|   | Triglyceride of octanoic and decanoic acid | 10 g |   |
|   | Ozokerite                                  | 2 g  |   |
|   | Water+acetic acid                          | 50 g |   |

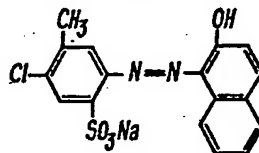
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## EXAMPLE E:

A cheek make-up is prepared according to the invention:

|    |                              |        |    |
|----|------------------------------|--------|----|
|    | Copolymer No. 10             | 15 g   |    |
|    | Stringy vaseline             | 6 g    |    |
|    | 2-Octyl-dodecanol-1          | 2 g    |    |
| 15 | Isopropyl palmitate          | 5 g    | 15 |
|    | Diisopropyl adipate          | 37.4 g |    |
|    | Candellila wax               | 2.5 g  |    |
|    | Carnauba wax                 | 2 g    |    |
|    | D and C Red No. 8 (dyestuff) |        |    |

20



20

... 0.5 g

|  |                |       |
|--|----------------|-------|
|  | Red iron oxide | 0.1 g |
|  | Titanium oxide | 1.5 g |
|  | Water          | 28 g  |

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## EXAMPLE F:

A moisturising milk for protection against sunburn is prepared according to the invention:

|    |   |      |    |
|----|---|------|----|
|    | Copolymer No. 11  | 10 g |    |
|    | Triglyceride of octanoic and decanoic acid  | 6 g  |    |
| 30 | Isopropyl myristate   | 11 g | 30 |
|    | Diisopropyl adipate   | 30 g |    |
|    | Ozokerite   | 2 g  |    |
|    | "Parsol-Ultra" sold by Messrs. GIVAUDAN (a mixture of aminobenzoic acid esters and substituted cinnamic acid esters; filter for sunlight) | 2 g  |    |
| 35 | Water+lactic acid (0.6 g)   | 39 g | 35 |

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## EXAMPLE G:

A tinted "open air" cream is prepared according to the invention:

|    |                                 |      |    |
|----|---------------------------------|------|----|
|    | Copolymer No. 13                | 10 g |    |
|    | Isopropyl palmitate             | 7 g  |    |
|    | Diisopropyl adipate             | 28 g |    |
| 45 | Paraffin oil                    | 6 g  | 45 |
|    | Beeswax                         | 2 g  |    |
|    | Red iron oxide                  | 1 g  |    |
|    | Yellow iron oxide               | 1 g  |    |
|    | Titanium oxide                  | 1 g  |    |
| 50 | Water+hydrochloric acid (0.7 g) | 44 g | 50 |

**EXAMPLE H:**

A cuticle cream is prepared according to the invention:

|   |                     |    |   |   |
|---|---------------------|----|---|---|
|   | Copolymer No. 16    | 7  | g |   |
|   | Isopropyl palmitate | 20 | g |   |
| 5 | Perhydrosqualene    | 30 | g | 5 |
|   | Stringy vaseline    | 7  | g |   |
|   | Carnauba wax        | 3  | g |   |
|   | 2-Octyl-dodecanol-1 | 3  | g |   |
|   | Water               | 30 | g |   |

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**EXAMPLE I:**

An "oil-in-water" make-up remover cream is prepared according to the invention:

|    |  |    |   |    |
|----|--|----|---|----|
|    | Copolymer No. 18                           | 6  | g |    |
|    | Triglyceride of octanoic and decanoic acid | 18 | g |    |
| 15 | Isopropyl palmitate                        | 5  | g | 15 |
|    | Paraffin oil                               | 2  | g |    |
|    | Water                                      | 69 | g |    |

**EXAMPLE J:**

A cream of the following composition is prepared according to the invention:

|    |                         |    |   |    |
|----|-------------------------|----|---|----|
| 20 | Copolymer No. 9         | 15 | g | 20 |
|    | Phenyl-ether alcohol    | 40 | g |    |
|    | Diisopropyl adipate     | 7  | g |    |
|    | Water+acetic acid (4 g) | 38 | g |    |

**EXAMPLE K:**

A cream of the following composition is prepared according to the invention:

|    |                       |    |   |    |
|----|-----------------------|----|---|----|
|    | Copolymer No. 6       | 13 | g |    |
|    | Diisopropyl palmitate | 5  | g |    |
|    | 2-Octyl-dodecanol-1   | 5  | g |    |
|    | Stringy vaseline      | 1  | g |    |
| 30 | Diisopropyl adipate   | 26 | g | 30 |
|    | Ozokerite             | 2  | g |    |
|    | Water                 | 42 | g |    |

**EXAMPLE L:**

A cream of the following composition is prepared according to the invention:

|    |                  |      |   |    |
|----|------------------|------|---|----|
| 35 | Copolymer No. 3  | 10   | g | 35 |
|    | Perhydrosqualene | 25   | g |    |
|    | Stringy vaseline | 14.5 | g |    |
|    | Ozokerite        | 3    | g |    |
|    | Water            | 47.5 | g |    |

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The emulsions according to the invention are particularly suitable for the preparation of foundation creams, make-up and hand creams.

Of course the embodiments of the invention which have been described are given merely by way of illustration and numerous modifications are possible. In particular it is clear that it is possible to use several emulsifiers according to the invention simultaneously, optionally together with other previously known emulsifiers.

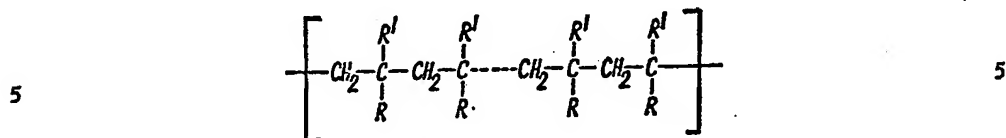
It is also obvious that all the ingredients usually employed, and in particular those which tend to improve the stability and shelf life of the emulsions, can be introduced into the emulsions according to the invention. Finally, it will be understood that the emulsions according to the invention can also be used in fields other than those of cosmetics and of excipients for pharmaceutical products.

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## WHAT WE CLAIM IS:—

1. An emulsion of the "water-in-oil" or "oil-in-water" type which comprises, as emulsifier, at least one sequence polymer (as hereinbefore defined), which contains (i) at least one lipophilic sequence corresponding to the formula:

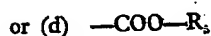
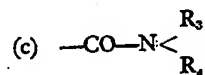


in which:

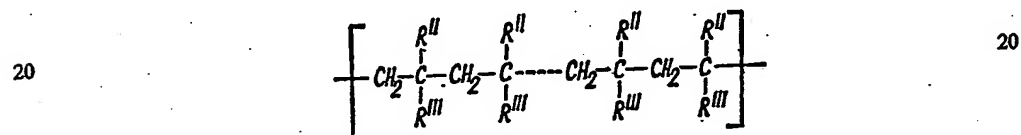
R represents a radical of the formula:



10 in which case R' represents a hydrogen atom, or

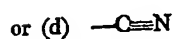
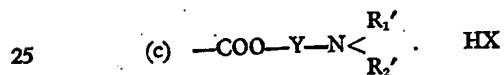
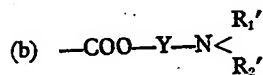
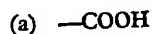


15 in which case R' represents a methyl radical,  
each of R<sub>1</sub> and R<sub>2</sub>, which may be the same or different, represents a hydrogen atom or an alkyl radical with 1 to 4 carbon atoms,  
R<sub>3</sub> represents a saturated hydrocarbon chain of 6 to 18 carbon atoms,  
R<sub>4</sub> represents a methyl or ethyl radical, and  
R<sub>5</sub> represents a saturated hydrocarbon chain of 5 to 26 carbon atoms,  
and (ii) at least one hydrophilic sequence corresponding to the formula:



in which:

R'' represents a radical of the formula:



in which case R''' represents a methyl radical,



5



10 in which case R''' represents a hydrogen atom  
each of R<sub>1</sub>' and R<sub>2</sub>', which may be the same or different, represents a hydrogen  
atom or an alkyl radical with 1 to 4 carbon atoms,

10

Y represents a saturated hydrocarbon chain of 2 to 4 carbon atoms, optionally  
containing one or more chain hetero-atoms, and

15 HX represents hydrochloric acid, hydrobromic acid, lactic acid or acetic acid.

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2. An emulsion according to Claim 1 wherein Y represents a saturated hydro-  
carbon chain of 2 to 4 carbon atoms containing at least one chain oxygen or sulphur  
atom.

3. An emulsion according to Claim 1 or 2 wherein R'' represents a carboxylic  
acid group which has been neutralised with an inorganic or organic base.

20 4. An emulsion according to Claim 1 or 2 wherein R'' represents a carboxylic  
acid group which has been salified by a sodium, potassium or magnesium salt.

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5. An emulsion according to any one of the preceding claims wherein the hydro-  
philic sequence is derived from 2-vinylpyridine, its hydrochloride or lactate, 4-vinyl-  
pyridine, its hydrochloride or lactate, *para*-dimethylaminostyrene, its hydrochloride or  
lactate, 2-(N,N-dimethylamino) ethyl methacrylate, 2-(N,N-diethylamino) ethyl meth-  
acrylate, 2-(N,N-dimethylamino) ethyl-glycol methacrylate, 2-(N,N-diethylamino)  
ethyl-glycol methacrylate or methacrylonitrile.

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6. An emulsion according to one of the preceding Claims wherein the hydrophilic  
sequence contains tertiary amine groups which are quaternised.

30 7. An emulsion according to Claim 8 wherein the hydrophilic sequence is quater-  
nised by dimethyl sulphate, ethyl bromide or  $\beta$ -bromoethanol.

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8. An emulsion according to any one of the preceding claims wherein the lipo-  
philic sequence is derived from styrene, 4-methylstyrene or lauryl methacrylate.

9. An emulsion according to any one of the preceding claims, wherein the sequence polymer has a molecular weight of between 1,000 and 1,000,000.

10. An emulsion according to Claim 9 wherein the sequence polymer has a molecular weight of between 8,000 and 700,000.

11. An emulsion according to any one of the preceding claims wherein the emulsifier is present in an amount between 5 and 20% by weight.

12. An emulsion according to any one of the preceding claims wherein the amount of emulsifier relative to the oil, and wax if present, is at least 10% by weight.

13. An emulsion according to any one of the preceding claims wherein the amount of oil, and wax if present, is between 20 and 65% by weight based on the weight of the emulsion.

14. An emulsion according to any one of the preceding claims wherein the amount of water is between 20 and 75% by weight.

15. An emulsion according to any one of the preceding claims, wherein the "oil" phase comprises at least one hydrocarbon, vegetable or animal oil or at least one saturated ester which does not turn rancid and is penetrating to the skin.

16. An emulsion according to Claim 15 wherein the "oil" phase comprises at least one paraffin oil, perhydrosqualene, purcellin oil, caballine oil, pork fat, sweet almond oil, callophylum oil, olive oil, avocado oil, isopropyl palmitate, isopropyl myristate, ethyl palmitate, diisopropyl adipate or a triglyceride of octanoic or decanoic acid.

17. An emulsion according to any one of the preceding claims wherein the "oil" phase contains a carnauba wax, candellila wax, beeswax, microcrystalline wax or ozokerite.

18. An emulsion according to Claim 1 substantially as hereinbefore described.

19. A cosmetic composition which comprises an emulsion as claimed in any one of the preceding claims.

20. A composition according to claim 19 which also contains at least one conventional cosmetic adjuvant such that it is in the form of a moisturising cream, foundation cream, make-up composition, fluid cream, brilliantine or sunburn oil.

21. A composition according to claim 19 substantially as described in any one of Examples A to L.

22. A process for the preparation of a "water-in-oil" or "oil-in-water" emulsion as claimed in any one of claims 1 to 18 which comprises mixing the desired sequence polymer with the "oil" part at a temperature of about 150°C, adding the "water" part, previously heated to a temperature of about 80°C, to the mixture, heated to about 80°C, with stirring, and cooling the mixture to ambient temperature with stirring.

23. A process according to claim 22 wherein at least one of acetic acid, lactic acid and hydrochloric acid is added to the "water" part.

24. A process according to claim 22 or 23 wherein the emulsion is subsequently passed over a (triple) roll mill to refine it.

25. A process according to any one of claims 22 to 24 wherein the sequence polymer is prepared substantially as hereinbefore described.

26. An emulsion whenever obtained by a process as claimed in any one of claims 22 to 25.

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